



Faculty of Resource Science and Technology

**SYNTHESIS AND CHARACTERIZATION OF Co(II), Ni(II),
Cu(II) AND Zn(II) ION COMPLEXES WITH TETRADENTATE
N₂S₂/ N₂O₂ - DONOR LIGANDS**

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Bachelor of Science with Honours
(Resource Chemistry)
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SYNTHESIS AND CHARACTERIZATION OF Co(II), Ni(II), Cu(II) AND Zn(II) ION
COMPLEXES WITH TETRADENTATE N_2S_2 / N_2O_2 – DONOR LIGANDS

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This project is submitted in partial fulfillment of the requirements for
the degree of Bachelor of Science with Honours
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Faculty of Resource Science and Technology
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2006

DECLARATION

No portion of the work referred to this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.



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Resource Chemistry Programme

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Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Zn(II) Ion Complexes with Tetradentate N_2S_2/ N_2O_2 – Donor Ligands

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ABSTRACT

Several cobalt(II), nickel(II), copper(II) and zinc(II) complexes of Schiff base ligands, such as benzil-bis(thiosemicarbazone) and ethylenediamine-bis(2-hydroxyacetophenone) have been synthesized. The ligands and their transition metal complexes were characterized by means of elemental analysis, molar conductance values, UV-Visible and Fourier Transform Infrared (FTIR) spectroscopic studies. The spectral data suggested that the transition metal complexes are made up of two tetradentate ligands coordinating through N_2S_2/ N_2O_2 donor systems, respectively. The Schiff base ligands act as dinegative tetradentate donor towards in all the complexes. The probable structures of the complexes have been deduced on the basis of their analytical and spectroscopic data.

Key words: benzil-bis(thiosemicarbazone), ethylenediamine-bis(2-hydroxyacetophenone), spectroscopic studies, transition metal complexes.

ABSTRAK

Beberapa kompleks kobalt(II), nikel(II), kuprum(II) dan zink(II) daripada ligan Schiff bes, seperti benzil-bis(thiosemikarbazona) dan etilindiamina-bis(2-hidroksiasetofenona) telah disintesis. Ligan-ligan dan kompleks-kompleks logam peralihan masing-masingnya telah dicirikan secara analisis keunsuran, nilai konduktiviti molar, cahaya nampak-UV dan Infra Merah Transform Fourier (FTIR). Data-data spektral mencadangkan bahawa kompleks-kompleks logam peralihan terdiri daripada dua ligan tetradentat masing-masing membentuk ikatan melalui sistem penderma N_2S_2/ N_2O_2 . Ligan-ligan Schiff bes bertindak sebagai penderma tetradentat dinegatif dalam kesemua kompleks. Struktur kompleks-kompleks yang terhasil telah dicadangkan berdasarkan data spektroskopik dan analisis.

Kata kunci: benzil-bis(thiosemikarbazona), etilindiamina-bis(2-hidroksiasetofenona), data spektroskopik, kompleks-kompleks logam peralihan.

CHAPTER ONE

INTRODUCTION

1.1 Coordination Compounds and Ligands

Coordination compounds can be defined as the compounds that have one or more complexes because there are coordinate covalent bonds for the bonds between the metal ions and the ligands in the complexes. It can also be defined as a compound formed from a Lewis acid and a Brønsted base (Jones, 2002). This kind of compounds formation may be regarded as a reversible association of one or more metal ions and ligands occurring in solution. For example,



Ligand is defined as the neutral molecules or ions (usually anions) which are attached with central metal ion in complex compounds. In Lewis sense, the ligands act as Lewis bases (electron pair donors) and the central metal ion acts as a Lewis acid (electron pair acceptor).

Coordination complexes between metal ions and $\text{N}_2\text{S}_2/\text{N}_2\text{O}_2$ donor ligands exhibit different types of crystal structure, a broad spectrum of biological properties, including antibacterial and antiviral activities (Zahra *et al.*, 2005). Chemically, polydentate (tetradentate) ligands such as $\text{N}_2\text{O}_2/\text{N}_2\text{S}_2$ are of interest because of the presence of several potential donor atoms, their flexibility and their ability to coordinate in either neutral or deprotonated forms.

For examples, Ni(II) complex with N_2O_2 Schiff base ligands derived from salicylaldehyde have long been used as homogeneous catalysts (Santos *et al.*, 2000). The coordination chemistry of transition metal complexes with salen-type ligands has achieved a special status because of their O_2 -binding reactivity, redox chemistry, unusual magnetic and structural properties, as well as their usage as models for metalloproteins, as 'metalloligands' (Kasumov *et al.*, 2005). Besides, it is also because of the chemical or electrochemical reduction of electrophiles, such as alkyl and aryl halides and carbon dioxide (Azevedo *et al.*, 2002). Macrocyclic Schiff base ligands derived from thiosemicarbazide are of significant interest for their pharmacological properties as antibacterial and anticancer agents (Arquero *et al.*, 1998).

In view of the above, the present project's aim was dealt with the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes with the proposed N_2S_2 / N_2O_2 donor ligands.

1.2 Characteristic of N-donor ligands

The study of the coordination chemistry of nitrogen donor ligands has expanded to a major area of research since the past three decades. This is due to the significant contribution of nitrogen donor ligands to the development of modern coordination chemistry. Therefore, the range of nitrogen donors is more extensive than other donor atom.

Nitrogen donor ligands can be classified based on the hybridization of the nitrogen (N) atom, which is known as sp^3 , sp^2 and sp . For example, some of the sp^3 - hybridized nitrogen donor atoms are given in Figure 1.

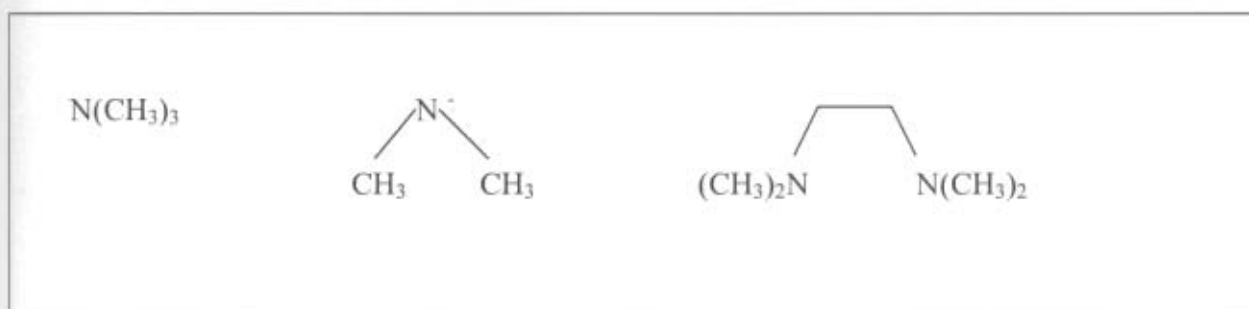


Figure 1: Some of the nitrogen donors with tertiary sp^3 - hybridized nitrogen (N) atoms

Complexes with nitrogen donor containing N-H bonds are normally not suitable for most of the organometallic reaction because an H atom on the coordination nitrogen is sufficiently acidic to react nucleophilically. Furthermore, coordinated nitrogen atom containing non-bonding pairs of electron is more susceptible to attack electrophile which is lack of electrons.

Ligands containing sp^2 - hybridized nitrogen atoms, mostly have very extensive coordination chemistry when then nitrogen (N) atom is a part of an aromatic system as listed in Figure 2. A much more extensive and functional coordination chemistry is possible when the ligands for this type of donor are bidentate or tetradentate. Nevertheless, the presence of stereogenic substituent is required for the use of such ligands in asymmetric catalysis.

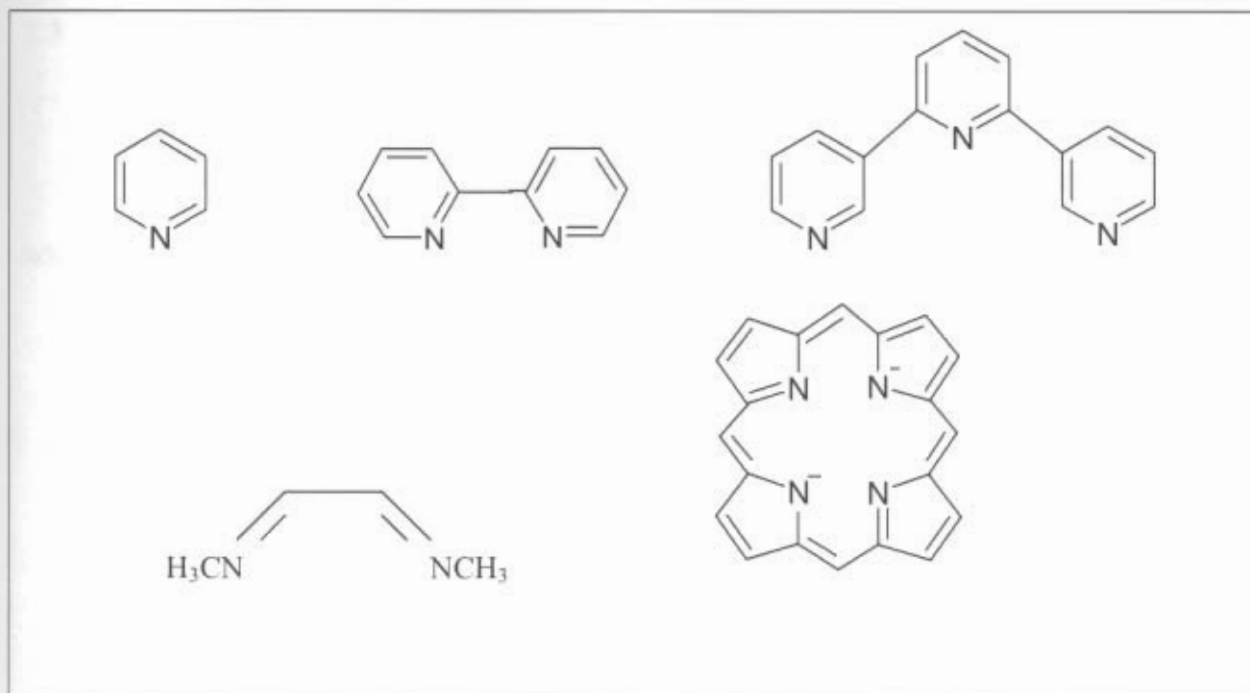


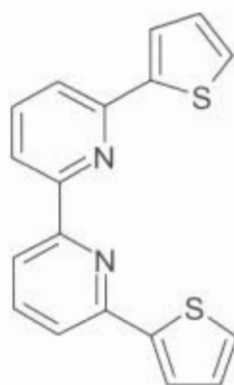
Figure 2: Some of the nitrogen donors with tertiary sp^2 - hybridized nitrogen (N) atoms

However, if there are C=N and C=C double bonds present in these molecules, it will render them for further reactions such as nucleophilic attack, or under suitable conditions hydrogenation which is true for Schiff bases. The only class of organic nitrogen donors with sp - hybridization is nitriles. Their major function is as labile ligands, which is weak and could be replaced by appropriate reagents. In addition, nitriles are quite liable towards nucleophilic attack once coordinated.

If only the nitrogen ligands relevant for organometallic chemistry, the conclusion will be that the nitrogen atoms in donor molecules, in coordination chemistry or in other branches of chemistry, could form strong bonds to the metal centers. The strength of the bonds is mainly depending on the covalence with a potentially significant contribution from the ionic character of the bond itself.

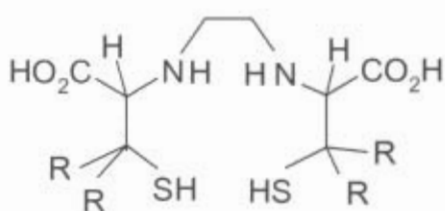
1.3 Tetradentate N_2S_2 – donor ligands

Tetradentate N_2S_2 ligand, 6,6'-bis(2''-thienyl)-bipyridine (**1.31**) which has two additional groups that may chelate has been described by Smith and Fraser (2004).

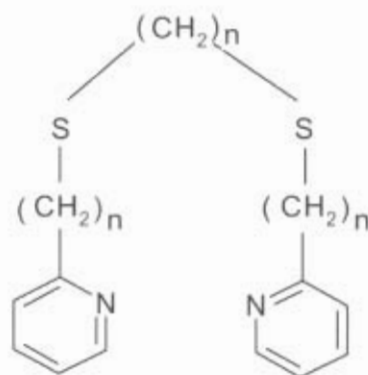


(1.31)

Another types of N_2S_2 donor ligand (**1.32**) that has been reported and described by Pettinari and Marchetti (2004). Pettinari and Marchetti (2004) have also described the synthesis of bis(pyridyl)-dithioether open-chain tetradentate ligand (**1.33**) which was obtained from the reaction of 2-(chloromethyl)pyridine and 1,n-alkanedithiols by standard procedures.



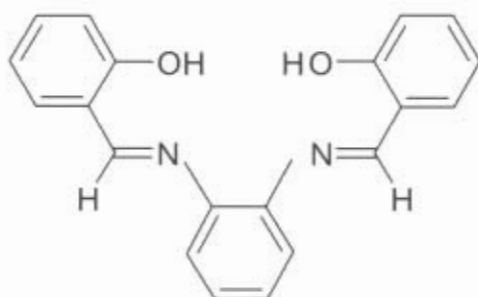
(1.32)



(1.33)

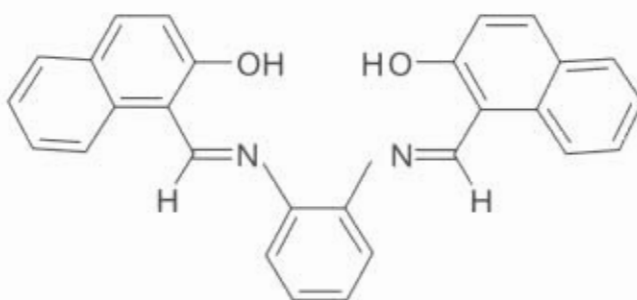
1.4 Tetradentate N_2O_2 – donor ligands

Tetradentate Schiff base ligands with a N_2O_2 donor atom set can be coordinated and are very well known to coordinate with various metal ions such as Co(II), Ni(II), Cu(II) and Zn(II). According to Abd-Elzaher (2001), three N_2O_2 donor ligands have been derived from the condensation reaction of *o*-phenylenediamine with salicylaldehyde, 2-hydroxy-1-naphthaldehyde and *o*-hydroxyacetophenone namely *N,N'*-bis(salicylaldehyde)*o*-phenylenediamine, *N,N'*-bis(2-hydroxy-1-naphthaldehyde)*o*-phenylenediamine and *N,N'*-bis(*o*-hydroxyacetophenone)*o*-phenylenediamine.



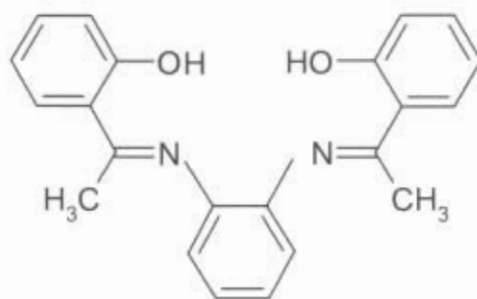
(SalophH₂)

N,N'-bis(salicylaldehyde)*o*-phenylenediamine (**1.41**)



(NophH₂)

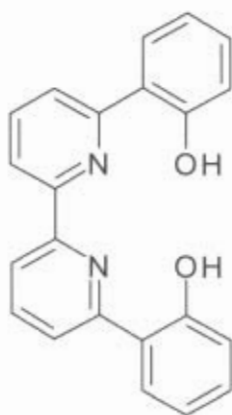
N,N'-bis(2-hydroxy-1-naphthaldehyde)*o*-phenylenediamine (**1.42**)



(AophH₂)

N,N'-bis(*o*-hydroxyacetophenone)*o*-phenylenediamine (**1.43**)

According to Smith and Fraser (2004), the tetradentate N₂O₂ ligand of 6,6'-bis(2-hydroxyphenyl)-bipyridine (**1.44**) has two additional groups that may chelate and has a yield of 90% which was prepared from 6,6'-diacetyl bipyridine and has been shown to be tetradentate in some copper complexes.



(**1.44**)

1.5 The Chelate Effect

Coordination compound which involving a chelating, multidentate ligand has an unusual stability as compared to the same coordination compounds which only involving monodentate ligand and is known as the chelate effect (Rodgers, 2002).



Overall stability constant, $\beta = 10^{10.6}$



Overall stability constant, $\beta = 10^{6.5}$ (Jones, 2002)

The overall stability constant, β for the complex $[\text{Cd}(\text{en})_2]^{2+}_{(\text{aq})}$ is almost 10^4 times greater compared to $[\text{Cd}(\text{MeNH}_2)_4]^{2+}_{(\text{aq})}$. This is due to the fact that the former complex contains chelate rings while the later one has no chelate ring.

1.6 Objective of the Project

The purposes of this research are:

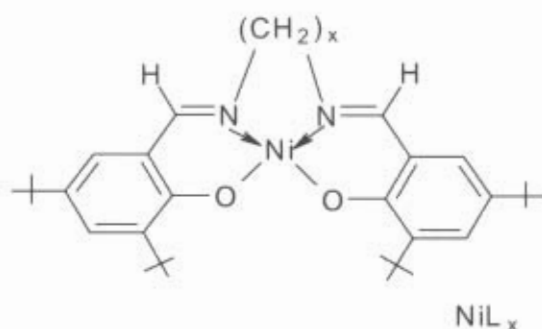
- i. To synthesize tetradentate N_2S_2 and N_2O_2 donor ligands.
- ii. To synthesize $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ ion complexes with tetradentate N_2S_2 and N_2O_2 donor ligands.
- iii. To identify the molar conductivity of these complexes.
- iv. To characterize tetradentate N_2S_2 and N_2O_2 donor ligands and their metal complexes by elemental analysis, UV-Visible and FTIR spectral studies.

CHAPTER TWO

LITERATURE REVIEW

2.1 Metal Complexes with N_2O_2 / N_2S_2 donor ligands

A series of N,N' - polymethylenebis(3,5-Bu^t₂-salicylalimine) ligands containing 2,4-di-Bu^t₂-phenol arms (Bu^t₂= di-*tert*-butyl), NiL_x and their Nickel(II) complexes (2.11) have been synthesized and characterized (Kasumov *et al.*, 2005).



(2.11)

H_2L_x	H_2L_1	H_2L_2	H_2L_3	H_2L_4	H_2L_5	H_2L_6
$(CH_2)_x$	$-(CH_2)_2-$	$-CH_2-\underset{\text{CH}_3}{\underset{ }{CH}}-$	$-(CH_2)_3-$	$-(CH_2)_4-$	$-(CH_2)_5-$	$-(CH_2)_6-$

Where

$H_2L_1 = N,N'$ - bis(3,5-Bu^t₂-salicylidene)-1,2-diaminoethane

$H_2L_2 = N,N'$ - bis(3,5-Bu^t₂-salicylidene)-1,2-diaminopropane

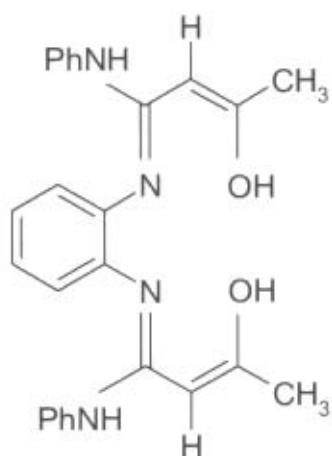
$H_2L_3 = N,N'$ - bis(3,5-Bu^t₂-salicylidene)-1,3-diaminopropane

$H_2L_4 = N,N'$ - bis(3,5-Bu^t₂-salicylidene)-1,4-diaminobutane

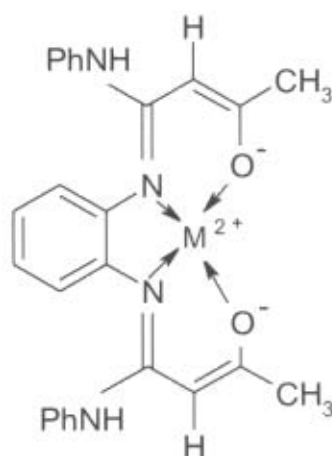
$H_2L_5 = N,N'$ - bis(3,5-Bu^t₂-salicylidene)-1,5-diaminopentane

$H_2L_6 = N,N'$ - bis(3,5-Bu^t₂-salicylidene)-1,6-diaminohexane

A new type of tetradentate ligand (**2.12**), which was reported by Raman *et al.* (2001), is formed by the condensation of *o*-phenylenediamine with acetoacetanilide. By coordinating the metal ion of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) in a tetradentate manner through the deprotonated hydroxyl group of the acetoacetanilide moiety and the azomethine nitrogen atoms of the Schiff base, the neutral tetradentate N₂O₂ complex is formed (**2.13**).



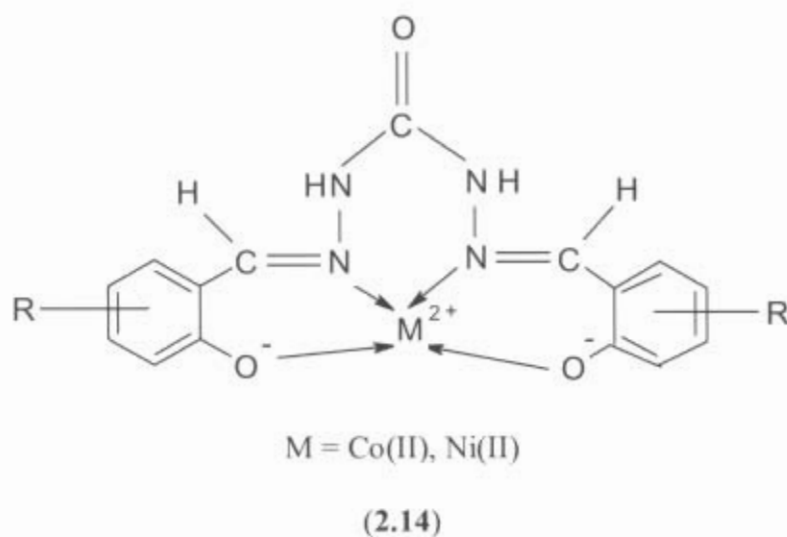
(2.12)



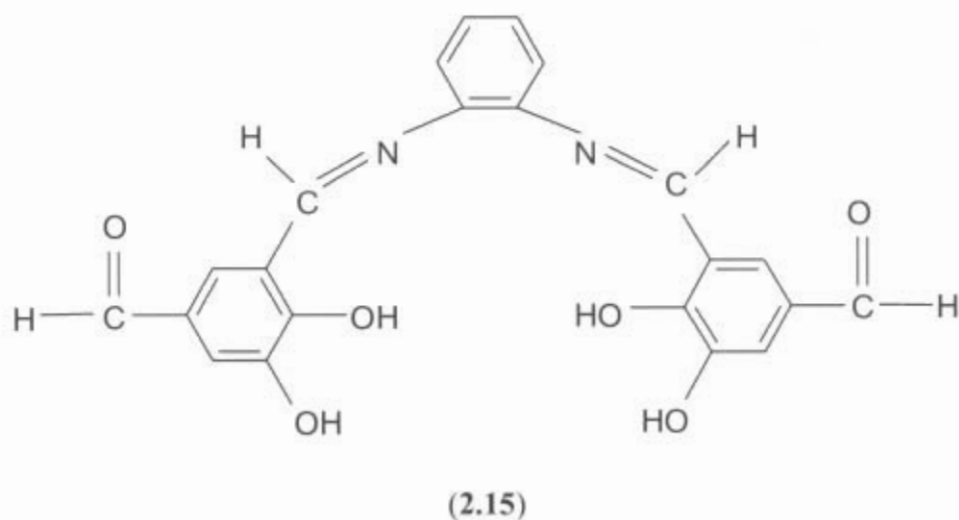
M = Cu(II), Ni(II), Mn(II), Zn(II) and VO(II)

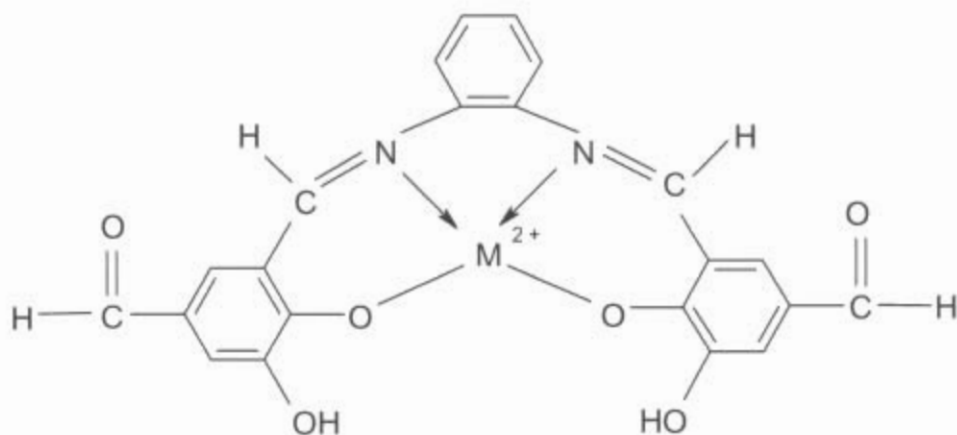
(2.13)

Warad and his co-workers (2000) reported the synthesis and characterization of Co(II) and Ni(II) complexes with tetradentate N_2O_2 ligand (2.14).



According to Kriza *et al.* (2001), the complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions with the new Schiff base (2.15) have been reported and the proposed structure for the compound is shown as (2.16).

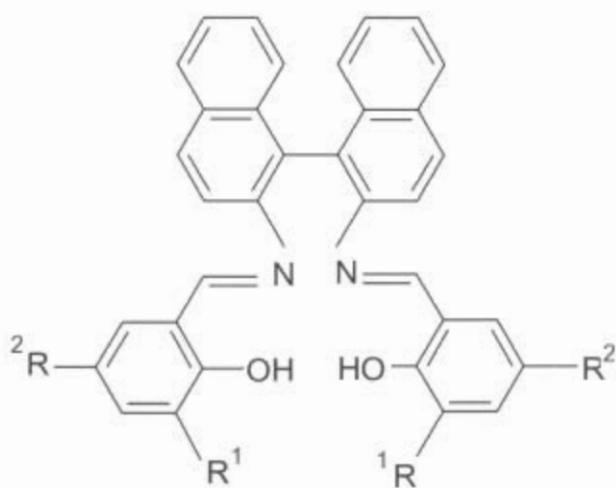




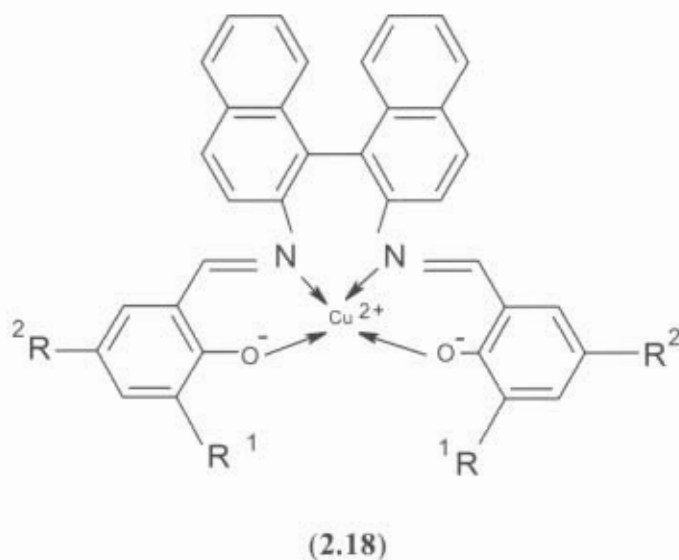
M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II)

(2.16)

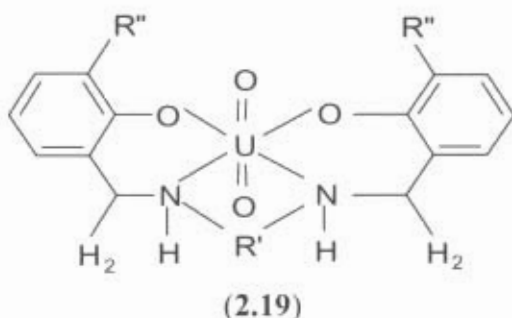
A chiral Schiff bases, 2,2'-bis (3- R^1 -5- R^2 -2-hydroxybenzylideneamino)-1,1'-binaphthyl (**2.17**), and its copper(II) complex (**2.18**) has been prepared by Smith (1998). The crystal structure of the racemic form of the complex where (R^1 and R^2 = Cl) has been determined and the complex has been shown to be an active catalyst for the oxidation of alkenes by tert-butyl hydroperoxide (Smith, 1998).



(2.17)



A total of seven new tetradentate ligands which is known as the Mannich base ligands having ONNO and ONNNO coordinating groups have been synthesized *in-situ* and allowed to react with uranyl (U) to get the corresponding compound (2.19) (Gandhi and Kulkarni, 2000).



Where

N,N'-bis(2-hydroxybenzyl)-1,2-diaminoethane, $R' = -CH_2CH_2-$; $R'' = H$

N,N'-bis(2-hydroxybenzyl)-1,2-diaminopropane, $R' = -CH_2C(CH_3)H-$; $R'' = H$

N,N'-bis(2-hydroxybenzyl)-1,3-diaminopropane, $R' = -CH_2CH_2CH_2-$; $R'' = H$

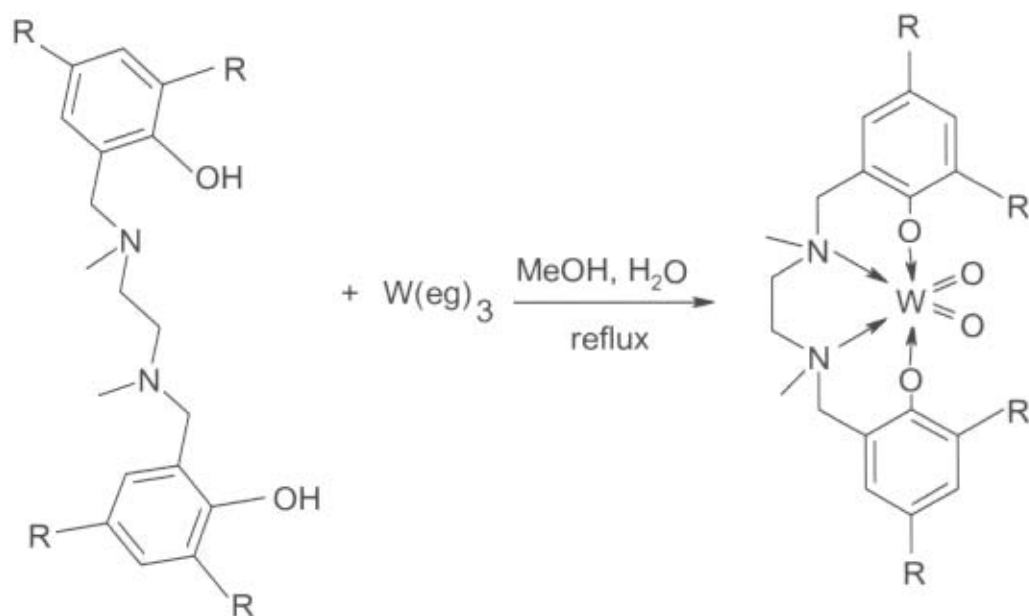
bis(2-hydroxybenzylaminoethyl)amine, $R' = -(C_2H_4)_2NH-$; $R'' = H$

N,N'-bis(2-hydroxybenzyl)-1,2-diaminobenzene, $R' = -C_6H_4-$; $R'' = H$

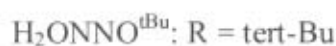
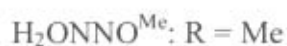
N,N'-bis(2-hydroxy-3-methoxybenzyl)-1,2-diaminopropane, $R' = -CH_2C(CH_3)H-$; $R'' = -OCH_3$

bis(2-hydroxy-3-methoxybenzylaminoethyl)amine, $R' = -(C_2H_4)_2NH-$; $R'' = -OCH_3$

Synthesis and spectral characterization of two new dioxotungsten(VI) complexes with ONNO donor ligand (**2.20**) have been described by Lehtonen (2005).

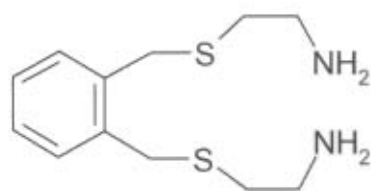


Where eg = 1,2-ethanediolate

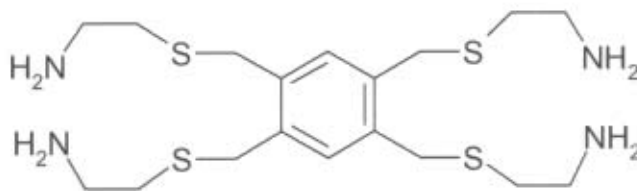


(**2.20**)

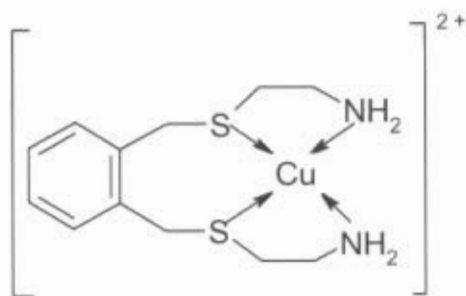
1,2-bis(1'-amino-3'-thiabutyl)benzene (**2.21**) and 1,2,4,5-tetrakis(1'-amino-3'-thiabutyl)benzene (**2.22**) have been synthesized and their copper(II) complexes (**2.23-2.24**) have been reported by De Iuliis *et al.* (2000).



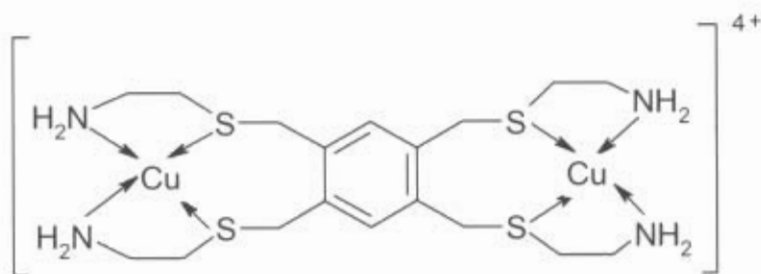
(**2.21**)



(**2.22**)



(2.23)



(2.24)

Two new N_2S_2 ligand which was prepared namely methyl-2-amino-1-cyclopentenedithiocarboxylate and N,N' -pentamethylene-bis(methyl-2-amino-1-cyclopentenedithiocarboxylate). Methyl-2-amino-1-cyclopentenedithiocarboxylate formed planar complexes with the metal ions of Cu(II), Ni(II) and Zn(II) in which they chelate as a bidentate ligand through a thioketonate sulfur and an imine nitrogen, while N,N' -pentamethylene-bis(methyl-2-amino-1-cyclopentenedithiocarboxylate) coordinates as a tetradentate ligand with the metal ions of Cu(II) and Ni(II) in a pseudo-tetrahedral coordination geometries where the pentamethylene bridge between the nitrogens introduces steric strain forcing distortion of the inner coordination sphere (Martin and Bereman, 1991).

Recently, Joseph *et al.* (2005) have synthesized and characterized a series of copper(II) complexes with N_2S_2 donor ligand which was 2-benzoylpyridine $N(4)$ -phenyl

thiosemicarbazone. A survey of literature shows that several reports are available regarding transition metal complexes of such kind of ligands (Pettinari and Marchetti, 2004; Kasumov *et al.*, 2005).